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High Surf. Area Fischer-Tropsch Catalyst

Inventor(s):

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What is claimed is:

1. A catalyst for use in the Fischer-Tropsch process, said catalyst comprising at least one metal that is an efficient carbon monoxide adsorber and at least one promoter, said metal and said promoter being dispersed on a support to form a catalyst particle, said particle having a BET surface area of from about 100 m²/g to about 250 m²/g, and said metal and said promoter being dispersed on the support such that the crystallite size of the metal oxide is from about 40 Å to about 200 Å, and said particle having an essentially smooth, homogeneous surface morphology.

- 10 2. The catalyst of Claim 1 wherein said particle comprises from about 5 wt % to about 60 wt % cobalt, and from about 0.0001 wt % to about 1 wt % of a first promoter, and from about 0.01 wt % to about 5 wt % of a second promoter.
- 3. The catalyst of Claim 2 wherein said particle comprises from about 10 wt% to about 30 wt % cobalt, and from about 0.01 wt % to about 0.05 wt % of said first promoter, and from about 0.1 wt % to about 1 wt % of said second promoter.
 - 4. The catalyst of Claim 1 wherein said metal is selected from the group consisting of nickel, cobalt, iron, ruthenium, osmium, platinum, palladium, iridium, rhenium, molybdenum, chromium, tungsten, vanadium, rhodium, copper, zinc, and combinations thereof.
 - 5. The catalyst of Claim 4 wherein said metal is cobalt.

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The catalyst of Claim 1 wherein said promoter is selected from the group 6. consisting of boron, cerium, chromium, copper, iridium, iron, lanthanum, manganese, molybdenum, palladium, platinum, rhenium, rhodium, ruthenium, strontium, tungsten, vanadium, zinc, sodium oxide, potassium oxide, rubidium oxide, cesium oxide, magnesium oxide, titanium oxide, zirconium oxide, and other rare earth metals, such as scandium, yttrium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, and combinations thereof.

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- The catalyst of Claim 2 wherein said first promoter is selected from the 7. group consisting of palladium, platinum, ruthenium, rhenium, rhodium, iridium and a combination thereof; and said second promoter is selected from the group consisting of potassium, boron, cesium, lanthanum, cerium, strontium, scandium, yttrium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, palladium, platinum, ruthenium, rhenium, rhodium, iridium and combinations thereof.
- The catalyst of Claim 1 wherein said support is selected from the group 8. consisting of aluminum oxide, y-alumina, alumina monohydrate, alumina trihydrate, 20 alumina-silica, magnesium silicate, silica, silicate, silicalite, y-zeolite, mordenite, titania,

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thoria, zirconia, niobia, hydrotalcite, kieselguhr, attapulgite clay, zinc oxide, other clays, other zeolites and combinations thereof.

- 9. The catalyst of Claim 8 wherein said support is γ -alumina.
- 10. The catalyst of Claim 9 wherein said support has a particle size of from about 60 μ m to about 150 μ m, a surface area of from about 90 m²/g to about 210 m²/g, a pore volume of from about 0.35 ml/g to about 0.50 ml/g, and a pore diameter of from about 8 nm to about 20 nm.
- 11. A catalyst for use in the Fischer-Tropsch process, said catalyst comprising cobalt dispersed on a support to form a catalyst particle, said particle being formed by the steps of:
- a) adding said support to water, with agitation, to form a slurry, and maintaining a slurry temperature at from about 35°C to about 210°C;
- b) adding an aqueous cobalt salt solution having a pH value greater than the point of zero charge of said support to said slurry with agitation and while maintaining said slurry temperature at from about 65°C to about 120°C;
- c) agitating said slurry and maintaining said slurry temperature at from about 65°C to about 120°C until said cobalt salt is essentially completely reacted with said support;
 - d) separating said slurry into a solid portion and a liquor portion;

washing said solid portion with water; e)

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- drying and calcining said solid portion at from about 90°C to about 375°C f) to form catalyst particles; and
- g) reducing said catalyst particles by heating said particles from ambient temperature to from about 300°C to about 500°C at a rate of from about 0.1°C/min to about 10°C/min over a period of from about 5 hours to about 40 hours.
 - The catalyst of Claim 11 wherein said support is selected from the group 12. consisting of aluminum oxide, y-alumina, alumina monohydrate, alumina trihydrate, alumina-silica, magnesium silicate, silica, silicate, silicalite, y-zeolite, mordenite, titania, thoria, zirconia, niobia, hydrotalcite, kieselguhr, attapulgite clay, zinc oxide, other clays, other zeolites and combinations thereof.
 - The catalyst of Claim 12 wherein said support is aluminum oxide. 13.
 - The catalyst of Claim 12 wherein said support has a particle size of from 14. about 60 µm to about 150 µm, a surface area of from about 90 m²/g to about 210 m²/g, a pore volume of from about 0.35 ml/g to about 0.50 ml/g, and a pore diameter of from about 8 nm to about 20 nm.

The catalyst of Claim 11 wherein said cobalt salt solution comprises water 15. and a cobalt (II) complex having coordination sphere ligands selected from the group

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consisting of water, chloride ion, ammonia, pyridine, triphenylphosphine, 1,2diaminoethane, diethylenetriamine, triethylenetetraamine, acetate, oxalate, 2,4pentanedione, ethylenedinitilo tetraacetic acid, and combinations thereof.

- The catalyst of Claim 15 wherein said cobalt (II) complex has 5 16. coordination sphere ligands selected from the group consisting of water molecules, ammonia, pyridine, diaminoethane, diethylenetriamine, triethylenetetraamine, and a combination thereof.
 - The catalyst of Claim 16 wherein said cobalt (II) complex is hexaammine 17. cobalt (II) carbonate.
 - 18. The catalyst of Claim 11 wherein the slurry temperature is maintained at from about 65°C to about 120°C in step a).
 - The catalyst of Claim 11 wherein said solid portion is dried at from about 19. 120°C to about 260°C in step f).
- The catalyst of Claim 11 wherein said particles are reduced in step g) by 20. heating said particles from ambient temperature to about 350°C at a rate of about 20 1.0°C/min and then holding said particles at about 350°C for from about 12 hours to about 16 hours.

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- The catalyst of Claim 11 wherein said particles are further stabilized to 21. prevent pyrophoric reactions when said particles are in the presence of air.
- The catalyst of Claim 21 wherein said particles are stabilized by being 5 22. coated with oil.
 - The catalyst of Claim 11 further including at least one promoter, said 23. promoter being added with said cobalt salt solution.
 - The catalyst of Claim 23 wherein said promoter is a metal salt selected 24. from the group consisting of rhenium (VII) oxide, ruthenium nitrosyl nitrate, platinum chloride, platinum ammine nitrate, platinum ammine chloride, and combinations thereof.
 - The catalyst of Claim 11 further including at least one promoter 25. impregnated onto said catalyst particle after said particle is dried in step f), said promoter being impregnated onto said particle by dipping said particle in an aqueous solution of said promoter while maintaining agitation, and then separating said impregnated particles from said solution, and drying said impregnated particles.
 - A method for making a catalyst for use in the Fischer-Tropsch process, 26. said catalyst comprising cobalt dispersed on a support to form a catalyst particle, said method comprising:

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- adding said support to water, with agitation, to form a slurry, and a) maintaining a slurry temperature at from about 35°C to about 210°C;
- adding an aqueous cobalt salt solution having a pH value greater than the b) point of zero charge of said support to said slurry with agitation and while maintaining said slurry temperature at from about 65°C to about 120°C;
 - agitating said slurry and maintaining said slurry temperature at from about c) 65°C to about 120°C until said cobalt salt is essentially completely reacted with said support;
 - separating said slurry into a solid portion and a liquor portion; d)
 - washing said solid portion with water; e)
 - drying and calcining said solid portion at from about 90°C to about 375°C f) to form catalyst particles; and
 - reducing said catalyst particles by heating said particles from ambient g) temperature to from about 300°C to about 500°C at a rate of from about 0.1°C/min to about 10°C/min over a period of from about 5 hours to about 40 hours.
 - The catalyst of Claim 26 wherein said support is aluminum oxide. 27.
- The catalyst of Claim 27 wherein said cobalt (II) complex is hexaammine 28. 20 cobalt (II) carbonate.

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The catalyst of Claim 26 wherein the slurry temperature is maintained at 29. from about 65°C to about 120°C in step a).

- The catalyst of Claim 26 wherein said solid portion is dried at from about 30. 120°C to about 260°C in step f). 5
 - The catalyst of Claim 26 wherein said particles are reduced in step g) by 31. heating said particles from ambient temperature to about 350°C at a rate of about 1.0°C/min and then holding said particles at about 350°C for from about 12 hours to about 16 hours.
 - The catalyst of Claim 26 wherein said particles are further stabilized by 32. being coated with oil.
 - The catalyst of Claim 26 further including at least one promoter, said 33. promoter being added with said cobalt salt solution.
 - The catalyst of Claim 33 wherein said promoter is a metal salt selected 34. from the group consisting of rhenium (VII) oxide, ruthenium nitrosyl nitrate, platinum chloride, platinum ammine nitrate, platinum ammine chloride, and combinations thereof.

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